PRODUCTS OF DETONATION OF TNT.¹

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The behavior of an explosive and the uses to which it may properly be put depend in a large measure on the form of the reaction or reactions it undergoes on explosion and the character of the products of these reactions. Its suitability for use as a propellant, as a bursting charge for shell, or as a blasting charge in demolitions, in land clearing, in mining and in other engineering operations is largely determined by the composition of its products, the rate at which they are evolved, and the temperature they acquire.

Among the explosives used largely during the recent war none more completely demonstrated its value and efficiency for use in H.E. shell, depth and drop bombs, mines and torpedoes, and for demolitions than TNT, either per se or, for fragmentation purposes, when mixed with ammonium nitrate or sodium nitrate to form the explosives styled amatol and sodatol. The authors from their investigations of the properties of the various surplus military explosives, which were assembled and being produced in large quantities as the armistice was declared, with a view to their utilization in civil undertakings, gave it as their opinion² that TNT, when used as directed, was especially suitable for use in the open. Returns from the National Park Service, Alaskan Engineering Commission, Reclamation Service, Bureau of Public Roads and the College of Agriculture of the University of Wisconsin, to each of which allotments of TNT have been made, and by whom it has been extensively used over a wide extent of area and under most varying climatic conditions, in quarrying, boulder breaking, ditch digging, land clearing and analogous operations, confirm this opinion. It

¹ Published by permission of the Director of the Bureau of Mines.

² U. S. Department of Agriculture Circular 94, of 1920: "TNT as a blasting explosive." Charles E. Munroe and Spencer P. Howell.

should however be stated that notwithstanding its excellent qualities the cost of manufacture will probably prevent TNT *per se* being used as a commercial explosive and that its use under the conditions noted above would not have been advised except for the necessity of promptly disposing of it and the lack of available funds to devote to its conversion into a more useful form.

As is pretty generally known, TNT is produced by the nitration of toluene but by such nitration, according to the way it is carried out, a large number of mono-, di- and tri-nitrotoluenes are produced. The existence of six different isomeric trinitrotoluenes is recognized as possible. By the methods now in commercial use the material which is produced in the largest quantity and in a pure, or nearly pure, condition is the α - or symmetric trinitrotoluene, and it is this material that was adopted as a military explosive and to which the distinctive name of TNT has been given. The criterion used for ascertaining the purity of TNT is its setting point after having been melted. Our War Department specifies for acceptance a S.P. of 80° C. for Grade I; of 79.5° C. for Grade II; and of 76° C. for Grade III. Grade I was produced in but small quantity especially for use in booster charges, though some was, perhaps unwisely, specified for demolition purposes.

The chemical reactions which TNT may undergo when exploded will differ with the circumstances under which it is exploded. When TNT is completely detonated unconfined much black smoke is given off, for not only are gases, and perhaps vapors, formed but carbon is set free. A theoretical expression for the reaction of the TNT *per se* is

(1) $2C_7H_5(NO_2)_3 \rightarrow I2CO + 5H_2 + 3N_2 + 2C.$

When TNT is completely burned with oxygen the reaction may run as follows

(2)
$$4C_7H_5(NO_2)_3 + 2IO_2 \rightarrow 28CO_2 + I0H_2O + 6N_2$$
.

From the presence of the easily ignitible and readily combustible gases, carbon monoxide and hydrogen, and of free carbon in expression (1) it is apparent that when these substances, in the highly heated condition they must be in at the time of explosion, come in contact with air they will ignite and burn, though there may not be time for their complete combustion, hence the results of the detonation of TNT in air under ordinary pressure would be represented partly by the first expression and partly by the second.

When the explosion takes place out of contact with air or oxygen in a confined space so that high pressures and temperatures are developed and maintained, the products first formed tend to dissociate or to react with one another to produce new associations so that, dependent on the primary reactions, the pressures and temperatures attained, and the rate of cooling, the kind of products, and the quantities of the several kinds of products will differ from those represented in (1) and (2). One such case may be represented by the expression

(3)
$$2C_7H_5(NO_2)_3 \rightarrow I2CO + 2CH_4 + H_2 + 3N_2$$
.

In practice TNT is exploded by a detonator, or, as in H.E. shell, by a primer and booster. Since TNT is less sensitive to detonation than dynamite, gun cotton and the better known high explosives it is advised that a No. 8 mercury fulminate, potassium chlorate detonator be employed to detonate it. Where "weaker" detonators, or those containing less than two grams of the detonant, have been employed to explode TNT in the open the explosive effect of the latter has been less and the smoke given off was grey.

In all cases detonators of some kind are used to explode TNT. They usually consist of copper capsules, which in the form of electric detonators are provided with copper leading wires and resistance bridges sealed in by sulphur plugs, and they are charged with determined weights of mercuric fulminate alone, or mercuric fulminate and potassium chlorate mixed, or mercuric fulminate and a tetryl booster, or with lead azide or other detonant, and on explosion they will give rise to gaseous and other products which will be mingled with the products from the TNT itself. It is true that the weight of the charge of detonant is, as a rule, but a small fraction of the weight of the TNT charge detonated but in any precise investigation of the products of detonation of TNT the products from the detonator used should be taken into account.

Although solid explosives, such as TNT is, when employed for

industrial purposes may be loaded directly into the bore holes yet experience has shown that convenience, economy and safety are promoted by using them in cartridge form. However, it has been demonstrated at the Bureau of Mines Experiment Station that the materials of the cartridge wrapper and the amounts used must be carefully considered since when combustible, as in industrial practice they usually are, they play a part in the reactions taking place on explosion and modify the kind and quantity of the gaseous products. Careful attention is now given to this matter of the wrapper in the preparation of explosives to pass the tests of Permissible Explosives since, by the nature of the tests they must pass, the quantity of inflammable and combustible, and, by regulation, that of the poisonous gases in the product must not exceed a fixed limit, nor may those of the explosive when in use in coal mines if it is desired that the explosive shall keep its place on the list of Permissibles.

Investigations of the products of explosion or detonation of TNT have been made by several observers. The earliest record noted is by C. E. Bichel³ in his "Table III., 1904," where, in a list of data for a considerable number of explosives, under "Trinitro-toluol" the following products in per cents by weight are given:

	Per Cent.
Carbon monoxide	70.5
Carbon dioxide	3.7
Hydrogen	1.7
Nitrogen	19.9
Carbon	4.2
	100.00

G. Carlton Smith, on page 90 of his book⁴ cites the above analysis stating that the products analyzed were "from the complete explosion of the material under atmospheric pressure." Michele Giua⁵ cites the same data from Bichel and states "sotto l'azione di un detonatora di fulminato di mercurio (gr. 1.5 di detonatore)"

³ "New Methods of Testing Explosives," C. E. Bichel. Translated and edited by Axel Larsen. London, 1905.

4"TNT, Trinitrotoluenes and Mono- and Dinitrotoluenes; their Manufacture and Properties." New York, 1918, D. Van Nostrand Co.

⁵ "Chimica delle sostanze esplosive." Milan, 1919, Ulrico Hoepli. PROC. AMER. PHIL. SOC., VOL. LIX, M, JULY 23, 1920.

but neither of these authors state the source from which the information was drawn.

It is probable that the explosion from which the products reported were obtained was carried out in the form of explosion bomb known as Bichel's Pressure Gage which was described and illustrated by Bichel in his paper on "Untersuchung Methoden für Sprengstoffe"⁶ and also in the book translated by Larsen as already stated.

Data on the explosion products of trinitrotoluene is also given by Poppenberg and Stephan^{τ} who made use of a calorimeter bomb. They give the following description of their method of procedure:

The experiment was conducted as follows: The bore hole of a lead bomb was loaded with compressed explosive, and over this was placed a lead plate which fitted exactly, the cap projecting through a hole in the plate. For further tamping the bore hole of the lead bomb was filled with dried sand and the upper part then covered with a lead plate. In several experiments we used a leaden seal, which contained the primer, for tamping. After placing the leaden seal in the bore hole the edge of the bomb was still about 0.5 cm. higher; this was turned over under the steam hammer by means of an apparatus for this purpose, and thus a complete tamping was obtained.

When the porcelain bomb was used for the experiment, we first arranged the tamping with sand and then poured Wood's metal into the conical boring in order to obtain a perfect seal. After this the fuse wire was joined to a very thin, pliable and insulated copper wire, and the bomb, thus prepared, was set inside the large steel bomb with the aid of a wire noose. In order to prevent the lead from being forced into the gas outlet, this had to be covered with an iron plate. The thin copper wires of the fuse were fastened to the bomb-head and this was screwed into the bomb. After an evacuation of about 20 cm. mercury the charge was ignited. During the progress of the work, the temperature of the gases was lowered to such an extent that the silk insulation of the wire was never burned. Therefore it was possible to complete a determination of the carbon given off. The carbon was rinsed out of the bomb so far as possible and then burned to carbon dioxide. It occurred to us to conduct the blasting in the material in which the explosives in question are used, but it did not seem advisable to perform the experiment in this manner, because all other materials, lead and porcelain except, react with the explosion gases. Porcelain alone can be used for explosive compositions which are rich in oxygen, since lead oxidizes. Therefore, it is necessary to dry the bombs before igniting the contents in order to prevent the water from having any effect upon the actual combination.

⁶ Zeitschrift f. Berg-, Hutten- und Salinen-Wesen, 50, 669-89, 1902.

⁷ "Ueber die Zersetzung von Pulvern und Sprengstoffen," Zeitschrift für das gesamte Schiess und Sprengstoffwesen, 5, 291-6, 1910.

Following this procedure when the charging density in the bomb was about 0.2 the products of two trials gave respectively the following results on analysis:

	1. Per Cent.	II. Per Cent.
Carbon monoxide	59.01	60.60
Carbon dioxide	1.93	1.66
Methane	1.97	1.90
Hydrogen	20.50	20.80
Nitrogen	16.05	16.08
	99.46	101.04

In a further experiment in which the trinitrotoluene was exploded in a lead cylinder enclosed in the bomb Poppenberg and Stephan obtained

	Per Cent.
Carbon monoxide	46.02
Carbon dioxide	20.60
Methane	1.40
Hydrocarbons	1.08
Hydrogen	7.61
Nitrogen	21.83
Air	1.33
	99.87

In discussing their results Poppenberg and Stephan referring to an opinion advanced by Kast from a study of theoretical equations of decomposition of trinitrotoluene say: "Kast calls particular attention to the fact that no water is formed when trinitrotoluol is detonated; our experience does not correspond to this assertion. We could prove regularly the presence of water in quantities of 1.5 to 1.8 per cent. in the explosion products. According to Kast's equation, 23.4 percent. of hydrogen was to be found in the explosion products, but the analysis shows only 21 per cent. This fact indicates further that when trinitrotoluol is detonated water must be formed."

Relative to the "hydrocarbons" reported these authors say:

The large carbon and hydrogen concentration governs the formation of hydrocarbons, which probably come from previously formed acetylene (compare Pring and gas composition of the explosion products of ammonal). The quantity, 1.08 per cent., is not significant and will not have any real effect on the explosion constants. Whether or not their formation affects the maximum pressure, that is, whether they are formed at the moment of explosion

or not until later, we will leave undecided. When analyzing the gas one naturally has to absorb these hydrocarbons first by means of bromine and fuming sulphuric acid, for otherwise the methane determination will be incorrect. If the explosion gases are lead off through ammoniacal silver solution, a small precipitate is obtained which we claim to be acetylide. Moreover, the explosion gases contain in small quality products of the incomplete combustion, which probably account for their disagreeable sharp odor. We presume, on account of the color of fuchsine sulphurous acid, unsaturated aldehyde.

We found further, in the explosion gases of trinitrotoluol significant quantities of ammonia, about 6 per cent. We ascertained this while we were introducing the gases and the ammonia set free from the residue of the explosion by potash-lye, into standardized muriatic acid. The ammonia could have been formed, as Kast assumes, by direct combination of nitrogen and hydrogen. We are not willing to subscribe to this opinion, for then we should not be able to explain why only insignificant small quantities of ammonia are formed when picric acid is detonated. We are much more of the opinion, supported by Sabatier's experiments, that the ammonia is formed from nitric oxide and hydrogen. The nitric oxide must be formed in quantities which correspond to the equilibrium between oxygen and nitrogen. According to Sabatier⁸ $2NO + 2H_2 = N_2 + 2H_2O$ (I). But in the case of greater hydrogen concentration, ammonia is formed, $2NO + 5H_2 = 2H_2O$ +2NH₃ (II). In the case of picric acid only small quantities of hydrogen are contained in the explosion gases, therefore equation I is substantially realized. But in the case of trinitrotoluol the nitrogen present is converted into ammonia. These reactions occur with great speed; whether or not they are to be considered in arriving at the disintegration equation, later experiments will have to prove.

Bichel in his "Table III. of 1904" definitely states that the data presented there is given in percentages by weight. Smith in reporting the analyses of the different products of these experiments treats them as if they were stated all in the same terms whereas the results in the second and third experiments he cites appear to be stated in percentages by volume. Poppenberg and Stephan do not state the terms in which they report their results, evidently assuming that the results of the analysis of a gas will be understood as being given in percentages by volume since this is the usual custom, and an examination of the data justifies this opinion.

Taking the data of Bichel's experiment and subtracting the solid C the percentage by volume of the residual permanent gases under normal conditions may be found. The following result is thus obtained:

⁸ Ann. de phys. et chem., 1905, 319.

		Per Cent.
Carbon monoxide		60.32
Carbon dioxide		
Hydrogen		. 20.65
Nitrogen	• • • • • •	. 17.05

and it is seen that the composition nearly approaches that given for the products of Poppenberg and Stephan's experiments I. and II.

Bichel's experiment is the only one whose results admit of a comparison being made with TNT itself in order to ascertain the extent to which the two agree. For this purpose Bichel's percentages for the compound substances have been reduced to their elements, the total for each element assembled and the elementary composition of the products compared in the following with that of pure TNT.

ELEMENTARY COMPOSITION OF BICHEL'S PRODUCTS AND OF TNT BY WEIGHT.

	Bichel's Products.	TNT.	Difference.
Carbon	35.423	36.990	-1.567
Oxygen	42.977	42.277	+0.700
Hydrogen	1.700	2.219	-0.519
Nitrogen	19.900	18.509	+1.391
	100.000	99.995	

In the descriptions of the above investigations as found no description of the trinitrotoluene used or any means of checking it, such as melting point, setting point or other data appear. Poppenberg and Stephan do not state what kind of detonator was used, Giua notes that Bichel in his first experiment used 1.5 gram mercury fulminate detonator. Experience has shown that at least a No. 8 detonator containing 2 grams⁹ of the fulminate charge is essential to insure the full detonation of TNT, and the somewhat erratic results obtained in the pressure gage led us to consider the trial of tetryl detonators in the hope that more certain uniformity might result.

Considering the state of the information regarding the explosion products of trinitrotoluenes that we have found in the literature; the

⁹ "A Primer on Explosives for Metal Miners and Quarrymen," Charles E. Munroe and Clarence Hall. Bureau of Mines Bulletin 80, 1915, page 36.

fact that the Bureau of Mines Experiment Station possesses a Bichel Pressure Gage equipment with proper laboratory accessories which it has long made use of in its tests of explosives to determine their "Permissibility" and for other purposes, and a force experienced in their use; and that TNT is now readily accessible and possesses a special interest, it has been deemed proper to make a special investigation of the products of detonation of TNT. As the investigation will necessarily be somewhat prolonged we are presenting here practically a progress report giving the preliminary results.

The TNT at command from the war surplus gave a solidification point of 80.2°, and a nitrogen percentage by the Orndorff method of 18.14 and by the Dumas method of 18.32 both S.P. and N-content being used as criterions of purity, and the N-content being also used as a ready check on the completeness of the recovery of the products.

The Orndorff method of determining nitrogen devised by Prof. Orndorff of Cornell University and as yet unpublished, is briefly a modification of the Kjeldahl method in which red phosphorus and hydrogen iodide, together in some instances with iodine, is used as the reducing agent, and cupric sulphate, sodium sulphate and sulphuric acid as the digestion agent. This method has been quite generally used during and since the war and is much approved. The method gives quite concurrent results on explosive substances and from general considerations of all the circumstances it is believed to give results to about the same degree below the truth that the Dumas method does above.

The Bichel Pressure Gage equipment of the Bureau of Mines is described, with illustrations, on pages 103–109 of Bureau of Mines Bulletin 15¹⁰ and the procedure followed in its use on pages 30–32 of Bureau of Mines Technical Paper 186.¹¹ In early tests of explosives detonations were made in lead bombs enclosed in the gage after the manner described by Poppenberg and Stephan but this was found to injure the gage and alter its volume, hence the method was long since abandoned. A recent recalibration of both the 15- and 20-liter

¹⁰ "Investigations of Explosives Used in Coal Mines," Clarence Hall, W. O. Snelling, and S. P. Howell. 1912.

¹¹ "Method for Routine Work in the Explosives Physical Laboratory of the Bureau of Mines," S. P. Howell and J. E. Tiffany. 1918.

gages showed their volumes to be 15.3 and 20.6 liters respectively and these latter volumes are made use of here in ascertaining the loading or charging density. It is to be noted that the pressure in the gage is reduced to 50 ± 5 millimeters before the explosive is fired.

Unless otherwise stated a No. 8 electric detonator, containing in its copper capsule 2 grams of composition consisting of mercuric fulminate 80 per cent. and potassium chlorate 20 per cent., was used to detonate each charge of TNT.

As before stated the explosive used was Grade I TNT prepared for the Ordnance Department of the U. S. Army. The material was received in bulk and in preparing it for the gage the weighed charge was packed in a tinfoil wrapper. This tinfoil varied in weight from 1.5 grams on the 25 gram charge to 9 grams for the 400 gram charge of TNT.

The pressure of the permanent gases in the gage was measured on a calibrated Schaeffer and Buddenberg gage 5 minutes after firing the shot, and a differential sample of the gases drawn off over mercury for analysis one half hour after firing the shot, the temperature of the gage and the gases being read at the same time.

In those tests where a charge of 250 grams or more was used, the pressure of the gases was greater than the capacity of the Schaeffer and Buddenberg gage. Accordingly, in order to be able to make a reading, immediately after firing the shot, the gases were allowed to equalize in pressure between the 15-liter gage and a 20liter gage previously evacuated at 50 millimeter pressure, connected together for that purpose. The observed pressure reading in those tests is the pressure obtained in the two gages after equalization.

The gases were analyzed in the Burrell modification of the Orsat apparatus described as to its construction and operation by Burrell and Oberfall¹² being determined in the order CO_2 , O, CO, H, CH₄ and N, and the results of the analyses are presented as determined in percentages by volume.

¹² "The Use of Copper Oxide for Fractionation Combustion of Hydrogen and Carbon Monoxide in Gas Mixtures," G. A. Burrell and G. G. Oberfall. *Jour. Ind. Eng. Chem.*, 8, 228–31. 1916.

CALCULATIONS

A computation of the total amount of nitrogen in the gases compared with the total nitrogen in the explosive, detonator, and residual air in the gage, serves as a check on the accuracy of the observations involved. This computation is based on the following data:

> Analysis of gases, Weight of charge, Barometer, Absolute pressure in gage, Temperature in gage before shot, Temperature in gage after shot, Pressure of permanent gases.

The following complete calculation of test $\frac{M-2354}{P-1847}$ is given as an example of the method of calculation:

Analysis of Gases.		
	Per Ce	nt.
CO ₂	I.I	
0	.0	j
со	60.2	
н	21.0	,
СН,	I.0	
N	15.8	
Weight of charge	300	grams
Barometer reading	-	mm.
Absolute pressure in gage		mm.
Temperature of gages before shot.	5-	
(15 liter gage)	25°	C
(20 liter gage)	•	
Temperature of gages after shot.	-3	С.
(15 liter gage)	070	C
(19 liter gage)		
Lev much sase ,	27	14

Nitrogen in Explosive.

 $300 \times .1814 = 54.420$, in which 300 = weight in grams of explosive, 18.14 = per cent. N in TNT, as determined by the Explosives Chemical Laboratory by the Orndorff Method.

Nitrogen in Residual Air.

(1)

$$\frac{50 \times 15.3 \times .7904 \times 273 \times 1.2542}{760 \times 298} = .908,$$

in which 1.2542 = weight of 1 liter of N at 0° C. and 760 mm.,

 $\frac{50 \times 273 \times 15.3}{760 \times 298}$ = volume of air at 0° C. and

760 mm. left in 15 liter gage. 79.04 = per cent. N in air.

(2)

 $\frac{50 \times 20.6 \times .7904 \times 273 \times 1.2542}{760 \times 298} = 1.223,$

in which 1.2542 = weight of 1 liter of N at 0° C. and 760 mm.,

 $\frac{50 \times 273 \times 20.6}{760 \times 298}$ = volume of air at 0° C. and

760 mm. left in 20 liter gage.

79.04 = per cent. N in air.

Nitrogen in No. 8 Electric Detonator.

 $2 \times .80 \times .0985 = .158$ grams, in which 2 = weight of charge in grams, and 80 = per cent. mercury fulminate in charge, and 9.85 per cent. N in mercury fulminate.

Total N Put in Gage.

From	explosive	54.420	grams
From	residual air	2.131	grams
From	electric detonator	.158	grams
		56.709	grams

Nitrogen in Gaseous Products of Combustion.

Observed pressure gage reading, 8.05 kg. per sq. cm	5,925 mm. mercury
Barometer	
Total pressure in gages	6,657 mm. mercury

 $6657 \times .01832 = 121.96$, $6657 \times .02483 = 165.29$, 287.25 liters of gas from 300 grams explosive, in which 6657 = total pressure in gages in mm. of mercury, .01832 = factor to reduce to 0° C. and 760 mm. pressure $\frac{273 \times 15.3}{760 \times 300}$.02843 = factor to reduce to 0° C. and 760 mm. pressure $\frac{273 \times 20.6}{760 \times 298}$, $287.25 \times .158 \times 1.2542 = 56.922$ grams N in gases, in which 287.25 = liters of gas in both gages at 0° C. and 760 mm., 15.8 = per cent. N in gas, 1.2542 = weight of 1 liter of N at 0° C. and 760 mm.

N put in gage	
N found in gases	
Difference	+.213 grams

In order to compare directly the products of combustion from the explosive at different pressures, all of the gas analyses were computed free from the nitrogen in the residual air and that given off by the electric detonator. These results are given with each test and also in the summary in Table No. 2.

DETAILS OF TESTS.

Test No. $\frac{M - 2354}{P - 1834}$.

Weight of charge 25 grams.

Temperature of gage before shot 29° C.

Temperature of gage after shot 29° C.

Barometer, 728 mm.

Observed gage pressure 1.01 kg. per sq. cm.

CO2 CO H CH4	Per cent. 6.2 .0 51.5 26.1 .2 16.0	CO2 O CO H CH4 N.	Per cent. 6.4 .0 53.2 26.9 .2

Gas Analyses.

Calculations.

N in explosive, $25 \times .1814$ N in residual air N in No. 8 electric detonator	.896 grams
Total N put in gage	5.589 grams
N found in gases: Obs. pres. 1.01 kg. per sq. cm Barometer Abs. pres. in gage	728 mm.

 $1471 \times .01820 = 26.77$ liters gas from 25 grams. $26.77 \times .16 \times 1.2542 = 5.372$ grams N in gas.

N put in gage	
N found in gas	5.372 grams
Difference	—.217 grams

Test No. $\frac{M-2354}{P-1835}$. Weight of charge, 50 grams. Temperature of gage before shot 22° C. Temperature of gage after shot 23° C. Barometer, 734 mm. Observed gage pressure 2.88 kg. per sq. cm.

Gas	Analys	es.

As Found in Gage.		Calculated Free from N in Residual Air an Elec. Detonator.	
	Per cent.		Per cent.
CO2	5.0	CO2	5.1
0	.0	0	.0
CO	52.5	CO	53-3
H	27.1	H	27.6
CH4	•4	CH4	•4
N	15.0	N	13.6

Calculations.

N	in explosive, 50	★.1814	9.070	grams
N	in residual air .		.917	grams
Ν	in No. 8 electric	detonator	.158	grams
	Total N put in	gage	10.145	grams
N	found in gases:	Obs. pres. 2.88 kg, per sq. cm	2,120	mm.
		Barometer	734	mm.
		Abs. pres. in gage	2.854	mm.

 $2,854 \times .01859 = 53.06$ liters of gas. $53.06 \times .15 \times 1.2542 = 9.982$ grams N in gas.

N put in gage	10.145	grams
N found in gas	9.982	grams
Difference	163	grams

Test No. $\frac{M - 2354}{P - 1832}$. Weight of charge, 75 grams.

Temperature of gage before shot 27.5° C.

Temperature of gage after shot 28.0° C.

Barometer 732 mm.

Observed gage pressure 4.60 kg. per sq. cm.

Gas Analyses.

As Found in Gage.		Calculated Free from N in Residual Air and Elec. Detonator.	
	Per cent.		Per cent.
CO2	I.8	CO2	1.8
D	.0	0	.0
20	58.0	CO	58.7
I	24.8	H	25.1
CH4	.1	CH4	.1
N	15.3	N	14.3

Calculations.

N in explosive, $75 \times .1814$	13.605 grams
N in residual air	.899 grams
N in No. 8 electric detonator	.158 grams
Total N put in gage	
N found in gases: Obs. pres. 4.60 kg. per sq. cm	3,386 mm.
Barometer	732 mm
Abs. pres. in gage	4,118 mm.

 $4,118 \times .01826 = 75.19$ liters of gas.

75.19 × .153 × 1.2542 == 14.428 grams N in gas.

N put in gage	14.662 grams
N found in gas	14.428 grams
Difference	234 grams

Test No. $\frac{M - 2354}{P - 1833}$. Weight of charge 100 grams. Temperature of gage before shot 28° C. Temperature of gage after shot 28.5° C. Barometer 729 mm. Observed gage pressure 6.81 kg. per sq. cm.

Calculated Free from N in Residual Air and As Found in Gage. Elec. Detonator. Per cent. Per cent. CO2..... CO2.... 2.0 2.0 0..... 0..... .0 .0 CO..... CO..... 58.0 58.5 Н..... H 25.4 25.6 CH4..... CH4..... .I .I N 14.5 N 13.8

Gas Analyses.

Calculations.

N in explosive, 100 × .1814	18.140 grams
N in residual air	.899 grams
N in No. 8 electric detonator	.158 grams
Total N put in gage	19.197 grams
N found in gases : Obs. pres. 6.81 kg. per sq. cm	5,012 mm.
Barometer	729 mm.
Abs. pres. in gage	5,741 mm.

 $5741 \times .01826 = 104.83$ liters of gas. $104.83 \times .145 \times 1.2542 = 19.064$ grams N in gas.

N put in gage			
N found in gas	19.064	grams	
Difference	133	grams	

Test No. $\frac{M - 2354}{P - 1863}$. Weight of charge, 150 grams. Temperature of gage before shot 25° C. Temperature of gage after shot 26° C. Barometer 738 mm. Observed gage pressure 10.83 kg. per sq. cm.

As Found in Gage.		Calculated Free from N in Residual Air and Elec. Detonator.	
	Per cent.		Per cent.
CO2	I.4	CO2	I.4
0	.0	0	.0
со	58.1	CO	58.4
H	25.6	H	25.7
CH4	.5	CH4	.5
N	14.4	N	14.0°

Gas Analyses.

Calculations.

N in explosive, $150 \times .1814$	27.210 grams
N in residual air	.911 grams
N in No. 8 electric detonator	.158 grams
Total N put in gage	28.279 grams
N found in gases: Obs. pres. 10.83 kg. per sq. cm	7,971 mm.
Barometer	738 mm.
Abs. pres. in gage	8,70 <u>9</u> mm.

 $8709 \times .01838 = 160.07$ liters of gas. $160.07 \times 14.4 \times 1.2542 = 28.910$ grams N in gas.

N put in gage	28.279 grams
N found in gas	28.910 grams
Difference	+.631 grams

Test No. $\frac{M-2354}{P-1840}$. Weight of charge of 200 grams. Temperature of gage before shot 27° C. Temperature of gage after shot 28° C. Barometer 726 mm. Observed gage pressure 13.79 kg. per sq. cm.

As Found in Gage.		Calculated Free from N in Residual Air Elec, Detonator.	
	Per cent.		Per cent.
CO2	I.3	CO2	1.3
0	.0	0	.0
CO	59.7	CO	60.0
H	22.8	H	22.9
CH4	I.2	CH4	1.2
N	15.0	N	14.6

Gas Analyses.

Calculations.

N in explosive, $200 \times .1814$	36.280 grams
N in residual air	.899 grams
N in No. 8 electric detonator	.158 grams
Total N put in gage	37.337 grams
N found in gases: Obs. pres. 13.79 kg. per sq. cm	
Barometer	.726 mm.
Abs. pres. in gage	10.876 mm.

 $10876 \times .01825 = 198.49$ liters of gas. $198.49 \times .15 \times 1.2542 = 37.342$ grams N in gas.

N put in gage		
N found in gas	. 37.342	grams
Difference	+ 005	orams

Test No. $\frac{M - 2354}{P - 1841}$.

Weight of charge 250 grams.

Temperature of gages before shot 26° C.

Temperature of gages after shot, 15 liter, 28° C.; 20 liter, 26° C. Barometer 727 mm.

Observed gage pressure 6.69 kg. per sq. cm.

As Found in Gage.		Calculated Free from N in Residual Air an Elec. Detonator.	
	Per cent.		Per cent.
CO2	1.5	CO2	1.5
D	.0	0	.0
со	60.3	CO	60.7
Н	20.6	Н	20.7
СН4	I.9	CH4	2.0
N	15.7	N	15.1

Gas Analyses.

· Calculations.

N in explosive, 250 × .1814 45.3	50 grams
N in residual air	05 grams
N in No. 8 electric detonator	(5 grams
Total N put in gage 47.62	28 grams
N found in gases: Obs. pres. 6.69 kg. per sq. cm 4,92	
Barometer	27 mm.
Abs. pres. in gage 5,65	JI mm.

 $5651 \times .01826 = 103.17$ $5651 \times .02475 = 139.86$ 243.03 liters of gas. $243.03 \times .157 \times 1.2542 = 47.855$ grams of N in gas.

Test No. $\frac{M - 2354}{P - 1847}$.

Weight of charge 300 grams.

Temperature of gages before shot 25° C.

Temperature of gages after shot 15 liter, 27° C.; 20 liter 25° C. Barometer 732 mm.

Observed gage pressure 8.05 kg. per sq. cm.

Gas Analyses.

As Found in Gage.		Calculated Free from N in Residual Air and Elec, Detonator,	
CO ₂ O CO H	Per cent. I.I .0 60.2 21.0	CO ₂ O CO H	Per cent. I.I .0 60.6 21.1
CH4 N	1.9 15.8	CH4 N.	2.0 15.2

Calculations.

Ν	in	explosive, 300 × .1814	54.420	grams
N	in	residual air	.908	grams
N	in	residual air	1.223 .158	grams grams
	I	Cotal N put in gage	56.709	grams
N	fo	und in gases: Obs. pres. 8.05 kg. per sq. cm		
		Barometer		

 $6657 \times .01832 = 121.96$ $6657 \times .02483 = 165.29$ 287.25 liters of gas. $287.25 \times .158 \times 1.2542 = 56.922$ grams N in gas.

N put in gage	56.709	grams
N found in gas		-
Difference	+.213	grams

Test No. $\frac{M - 2354}{P - 1848}$

Weight of charge 350 grams.

Temperature of gages before shot 15 liter 25° C.; 20 liter 24° C. Temperature of gages after shot 15 liter 27° C.; 20 liter 24° C. Barometer 731 mm.

Observed gage pressure 9.48 kg. per sq. cm.

As Found in Gage.		Calculated Free from N in Residual Air an Elec. Detonator.	
	Per cent.		Per cent.
CO2	I.6	CO2	1.6
0	.0	0	0.
CO	60.5	CO	60.6
H	20.1	H	20.2
CH4	2.3	CH4	2.3
N	15.5	N	15.3

Gas Analyses.

Calculations.

N in explosive, $350 \times .1814$	63.490	grams
N in residual air	.908	grams
N in No. 8 electric detonator	.158	grams
Total N put in gage	64.556	grams
N found in gases: Obs. pres. 9.48 kg. per sq. cm	6,977	mm.
Barometer	731	mm.
Abs. pres. in gage	7,708	mm.

 $7708 \times .01832 = 141.21$ $7658 \times .02497 = 190.76$ } 331.97 liters of gas. $331.97 \times .155 \times 1.2542 = 64.535$ grams N in gas.

.N put in gage	64.556	grams
N found in gae	64.535	grams
Difference	021	grams

Test No. $\frac{M - 2354}{P - 1857}$.

Weight of charge 400 grams.

Temperature of gages before shot 15 liter 23° C.; 20 liter 22° C. Temperature of gages after shot 15 liter 25° C.; 20 liter 22° C. Barometer 731 mm.

Observed gage pressure 10.79 kg. per sq. cm.

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As Found in Gage.		Calculated Free from N i Elec. Detor	
	Per cent.		Per cent.
CO2	1.5	CO ₂	1.5
0	.0	0	.0
CO	60.4	CO	60.7
Н	19.8	H	19.9
CH4	2.3	CH4	2.3
N	16.0	N	15.6

Gas Analyses.

Calculations.

· Outernational
N in explosive, 400 × .1814 72.560 grams
N in residual air
1.231 grams
N in No. 8 electric detonator
Total N put in gage 74.863 grams
N found in gases: Obs. pres. 10.79 kg. per sq. cm 7,942 mm.
Barometer 731 mm.
Abs. pres. in gage 8,673 mm.
$8673 \times .01844 = 159.93$

$8673 \times .02508 = 217.52$	377.45	liters	of	gas	5.
377.45 × .16 × 1.2542=					

N	put in gage	74.863	grams
Ν	found in gas	75.744	grams
	Difference	+.881	grams

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TABLE I.

SUMMARY OF GAS ANALYSES AS FOUND IN GAGE, LITERS OF PERMANENT GASES AND NITROGEN CHECK USING ORNDORFF VALUES.

		Wt. of Charge (Grams).				
	25	50	75	100	150	
CO ₂ (per cent.)	6.2	5.0	1.8	2.0	1.4	
O (per cent.)	.0	.0	.0	.0	.0	
CO (per cent.)	51.5	52.5	58.0	58.0	58.1	
H (per cent.)	26.1	27.1	24.8	25.4	25.6	
CH4 (per cent.)	.2	•4	.1	.I	•5	
N (per cent.)	16.0	15.0	15.3	14.5	14.4	
Liters of gas	26.77	53.06	75.19	104.83	160.07	
N check (grams)	217	163	224	121	+.631	
	200	250	300	350	400	
CO ₂ (per cent.)	I.3	1.5	I.I	1.6	1.5	
O (per cent.)	.0	.0	.0	.0	.0	
CO (per cent.)	59.7	60.3	60.2	60.5	60.4	
H (per cent.)	22.8	20.6	21.0	20.1	19.8	
CH4 (per cent.)	I.2	1.9	1.9	2.3	2.3	
N (per cent.)	15.0	15.7	15.8	15.5	16.0	
Liters of gas	198.49	243.03	287.25	331.97	377.45	
N check (grams)	+.005	+.227	+.213	021	+.881	

	Wt. of Charge (Grams).				
	25	50	75	100	150
CO2 (per cent.)	6.4	5.1	I.8	2.1	I.4
O (per cent.)	.0	.0	.0	.0	.0
CO (per cent.)	53.2	53.3	58.7	59.8	58.4
H (per cent.)	26.9	27.6	25.1	26.2	25.7
CH ₄ (per cent.)	.2	.4	.I	.ι	.5
N (per cent.)	13.3	13.6	14.3	13.8	14.0
Loading density	$\frac{1}{612.0}$	$\frac{1}{288\cdot 1}$	$\frac{1}{185.7}$	$\frac{1}{140.3}$	$\frac{1}{92.72}$
	200	250	300	350	400
CO ₂ (per cent.)	1.3	1.5	I.I	1.6	1.5
O (per cent.)	.0	.0	.0	.0	.0
CO (per cent.)	60.0	60.7	60.6	60.6	60.7
H (per cent.)	22.9	20.7	21.1	20.2	19.9
CH_4 (per cent.)	1.2	2.0	2.0	2.3	2.3
N (per cent.)	14.6	15.1	15.2	15.3	15.6
Loading density	$\frac{1}{66.23}$	$\frac{1}{56 \cdot 87}$	$\frac{1}{42.86}$	1 38.0.5	$\frac{1}{33.25}$

TABLE II.

SUMMARY OF GAS ANALYSES CALCULATED FREE FROM NITROGEN IN RESIDUAL AIR AND ELECTRIC DETONATOR AND DENSITY OF LOADING.

NH₃ in Gaseous Products of Combustion.

Previous investigators of the products of combustion have reported varying amounts of NH_3 gas among the gaseous products of combustion of TNT, one investigator reporting as high as six per cent.

In carrying out these tests, a distinct but not strong odor of NH_3 was always obtained on opening up the gage after the shot. To determine the amount of NH_3 present in the gases, all the gases obtained from a 200 gram charge were passed through a dilute solution of sulphuric acid, and the amount of ammonia determined in this solution.

The test showed that the gas contained 0.034 per cent. of NH_3 . This value was that expected as the result of odor tests carried out by the Bureau of Mines which showed that an amount of NH_3 corresponding to 0.05 per cent. gave a strong odor of NH_3 .

EFFECT OF DENSITY OF CARTRIDGE OF TNT ON GASEOUS PRODUCTS.

In order to determine whether the density of the cartridge of TNT had any effect on the gaseous products of combustion of TNT,

tests were carried out using a 200 gram sample (M - 2630) of Grade I TNT, containing 18.34 per cent. nitrogen by the Orndorff method, which was obtained pressed to a density of 1.50, and the results obtained compared against a 200 gram sample of M - 2354, which was pressed to a density of 0.86.

The results of the tests are as follows:

Test No. $\frac{M-2354}{P-1840}$. Density of cartridge 0.86. Weight of charge 200 grams. Temperature of gage before shot 27° C. Temperature of gage after shot 28° C. Barometer 726 mm. Observed gage pressure 13.79 kg. per sq. cm.

As Found in Gage. Calculated		Calculated Free from N i Elec. Detor		
	Per cent.		Per cent.	
CO2	I.3	CO2	I.3	
D	.0	0	.0	
	59.7	CO	60.0	
ΗΕ	22.8	Н	22.9	
CH4	I.2 ·	CH4	I.2	
۶	15.0	N	14.6	

Gas Analyses.

Calculations.

N in explosive, 200 × .1814	36.280 grams
N in residual air	.899 grams
N in No. 8 electric detonator	.158 grams
Total N put in gage	37.337 grams
N found in gases: Obs. pres. 13.79 kg. per sq. cm	10,150 mm.
Barometer	726 mm.
Abs. pres. in gage	10,876 mm.

 $10876 \times .01825 = 198.49$ liters of gas.

 $198.49 \times .15 \times 1.2542 = 37.342$ grams N in gas.

N put in gage	37.337 grams
N found in gas	
Difference	+.005 grams

Test No. $\frac{M-2630}{P-1877}$. Density of cartridge 1.50. Weight of charge 200 grams. Temperature of gage before shot 25° C. Temperature of gage after shot 26° C. Barometer 718 mm. Observed gage pressure 13.51 kg. per sq. cm.

As Found in	Gage.	Calculated Free from N in Elec. Deton	
	Per cent.		Per cent.
CO2	0.9	CO2	0.9
0	.0	0	.0
со	59.1	CO	59.4
н	23.5	H	23.6
CH4	1.2	CH4	1.2
N	15.3	N	14.9

Gas Analyses.

Calculations.

N in explosive, $200 \times .1834$	36.680 grams
N in residual air	.914 grams
N in No. 8 electric detonator	.158 grams
Total N in gage	37.752 grams
N found in gases: Obs. pres. 13.51 kg. per sq. cm	9,943 mm.
Barometer	718 mm.
Abs. pres. in gage	10,661 mm.

 $10,661 \times .01838 = 195.95.$ $195.95 \times 15.3 \times 1.2542 = 37.601.$

N	put in gage	37.752 grams
Ν	found in gas	37.601 grams
	Difference	—.151 grams

TABLE III.

COMPARISON OF RESULTS SHOWING EFFECT OF DENSITY OF CARTRIDGE.

	Sample M	VI-2354	Sample M	-2630.
Density of cartridge	0.86	5	1.50)
Weight of charge	200	grams	200	grams

ANALYSIS OF GASES.

(1) As Found in Gage (Per Cent.).

CO ₂	1.3	0.9
0	.0	.0
со	59.7	59.1
Н	22.8	23.5
CH ₄	I.2	I.2
N	15.0	15.3

(2) Calculated Free from N in Residual Air and Electric Detonator (Per Cent.).

CO ₂	1.3	0.9
0	.0	.0
СО	60.0	59.4
Н	22.9	23.6
СН ₄	I.2	I.2
N	14.6	14.9
Absolute pressure in gage	10,876 mm.	10,661 mm.
Liters of gases	198.49	195.95
Nitrogen check	+.005 gms.	—.151 gms.

It will be noted from the above comparison that for equal weight of charge, the density of cartridge has no effect, within the experimental error, on the gaseous products of combustion of TNT.

Effect of Different Priming Substances on Products of Combustion of TNT.

In carrying out these tests, occasionally samples of gas were obtained using the same weight of charge which gave widely differing results from the usual results. As an example, there are given below three different analyses using a 400 gram charge.

	(1) <u>M-2354</u> <u>P-1849</u>	(2) <u>M-2354</u> P-1857	(3) M-2354 P-1855
	Per cent.	Per cent.	Per cent.
CO ₂	1.7	1.5	1.7
0	.0	.0	.0
CO	60.5	60.4	57.9
Н	19.3	19.8	23.6
CH4	2.4	2.3	1.9
N	16.1	16.0	14.9
Liters of permanent gases	378.21	377.45	411.33

It was thought that these different analyses were the result of the explosion reaction following different courses, and that if a priming charge different from mercury fulminate-potassium chlorate were used for initiating the detonation, the explosion reaction might either be made to always follow the same course or that a still different reaction might take place. Accordingly, tests were carried out using an electric tetryl detonator (M - 2664) containing a base charge of 1.2149 grams tetryl and a priming charge of .4650 grams mercury fulminate-potassium chlorate mixture.

The following table shows the composition of the gases obtained from 200 gram samples of M - 2354 at a density of 0.86 and 200 gram samples of M - 2630 at a density of 1.50, using both a fulminate and tetryl electric detonator. For comparative purposes, all these analyses have been computed free from the nitrogen in the residual air and electric detonators.

	Sample M-2354.		Sample M-2630.	
Test No Density Detonator	P-1840. 0.86. Fulminate.	P-1888. 0.86. Tetryl.	P-1878. 1.50. Fulminate.	P-1887. 1.50. Tetryl.
CO ₂	1.3	1.5	I.2	0.9
D	.0	.0	.0	.0
20	60.0	60.3	59.7	59.0
ΗΕ	22.9	22.2	22.9	23.3
CH4	1.2	I.8	I.2	1.7
N	14.6	14.1	15.0	15.1

It will be noted from the above table that the gases given off by the two samples of TNT were practically the same whether fulminate or tetryl detonators were used.

Solid Products of Combustion from Grade I TNT.

On opening up the Bichel gage after firing a charge of TNT, there is found deposited on the walls of the gage a very finely divided deposit of black soot-like appearing solid. This same solid can always be observed when TNT is detonated where the smoke can be seen.

The question has arisen as to the amount and composition of this deposit and its effect on the gases, *i.e.*, whether this carbon-like de-

posit would absorb a sufficiently large quantity of gases to influence the observed pressure reading for total quantity of gas produced, or absorb a selected gas in sufficiently large quantity to affect the composition of the gases.

On account of the rough and pitted condition of the interior of the Bichel gage, it was impossible to obtain an exact determination of the amount of this deposit. But several determinations were made to secure this as accurately as possible, and it was found that with 200 grams of M - 2354, 11 grams of solids were obtained, while from 400 grams, 15 grams were obtained, corresponding to 5.5 and 3.75 per cent. respectively. Two determinations made with 200 grams of M - 2630 gave 16 and 18.5 grams or 8.0 and 9.25 per cent. respectively.

While an insufficient number of tests have been carried out to warrant any definite conclusions, it would appear that the amount of deposit decreases with the increase in charge and is increased by the density of the cartridge, as in sample M - 2630 which was compressed to 1.50.

The exact composition of this deposit has not been determined as yet, for this deposit is contaminated by the iron from the support, copper and sulphur from the electric detonator, and tin from the wrapper holding the TNT, and no method so far tried has served to separate them. An analysis of the contaminated deposits has given the following result:

	Per Cent.
Moisture	0.25
Ash	77.10
Н	.33
С	34.34
N	1.01
S	3.97
0	.0

As the carbon, hydrogen and nitrogen are the elements in the deposit arising from the TNT, this analysis is recalculated eliminating the contaminating substances, and is as follows:

	er Cent.
H	 1.03
С	 6.07
Ν	 2.90
	-

In order to determine the nature and the quantity of gases absorbed by the solid products of combustion, two 400 gram charges were detonated in the Bichel gage.

Time.	Water.	Time.	Water.
9:44:30	0.0	59:00	6.6
9:47:30	13.0	59:30	6.6 ,
9:52:30	14.0	10:00:00	0.0
53:30	14.0	10:00 :30	3.3
54:30	14.0	01 :00	3.3
55:30	14.0	01 :30	3.3
56:00	0.0	02:00	3.3
56:30	5.0	02:30	0.0
57:00	6.4	03:00	I.2
57:30	6.5	03:30	I.3
58:00	6.5	04 :00	I.3
58:30	6.6	• 04 :30	1.3

M-2354 P-1849

1. After the differential sample of gas had been taken and the pressure in the gage was zero as shown by a water manometer, the gage was again closed up and readings taken every 30 seconds until the manometer reading was constant, when the pressure was again released and the readings repeated. The readings are given in the preceding table.

2. After the differential sample (a) had been taken for analysis and the pressure reduced to zero, the gage was again closed up and readings taken until there was no further increase in the pressure reading on the water manometer, when a second sample (b) of gas was taken and analyzed. The readings on the water manometer and the analyses of the two samples of gas (a and b) are given in the following tables on page 222.

In comparing the two gas analyses, it must be kept in mind that the amount of gas given off by the solid products of combustion was enough to change the analyses of all the gas remaining in the 15.3 liter gage to the extent given above.

When the gage was opened up, the solids in gage were collected and treated in a vacuum extraction apparatus to determine the composition of the gases still retained by these products. In calculating the analysis of the gas in the solids, the oxygen present was used as

1-1055				
Time.	Water, Cm.	Time.	Water, Cm.	
9:50:00	0.0	10:04:00	14.1	
51:00	6.5	04:30	14.2	
52:00	8.5	05:00	14.5	
52:30	9.0	05:30	14.6	
53:00	9.6	06:00	14.7	
53:30	9.9	06:30	14.9	
54:00	10.7	07:00	15.0	
54:30	10.9	07:30	15.0	
55:00	11.3	08:00	15.2	
55:30	11.6	08:30	15.3	
56:00	11.7	09:00	15.4	
56:30	11.9	09:30	15.5	
57:00	12.0	10:00	15.6	
57:30	12.2	10:30	15.7	
58:00	12.4	II:00	15.8	
58:30	12.8	12:00	15.9	
59:00	12.9	13:00	16.I	
59:30	13.0	14:00	16.3	
0:00:00	13.1	15:00	16.4	
00:30	13.3	16:00	16.6	
01:00	13.5	19:00	17.0	
01:30	13.6	38:00	18.5 •	
02:00	13.7			
02:30	. 13.8			
03:00	14.0			
03:30	14.1			

M—	-2354	
P -	-1855	•

Gas Analyses.

Per Cent.	Per Cent
CO ₂ I.7	2.7
0	.0
СО 57.9	57.9
Н 23.6	23.3
CH ₄ 1.9	1.9
N 14.9	14.2

the basis of determining the air content of the bottle and gases. This determination showed that each gram of solid products in the gage, including the iron, copper, tin and sulphur from the support, electric detonator and cartridge, retained 6.11 cubic centimeters of gas having a composition of:

P	er Cent.
CO ₂	71.3
0	.0
Н	.0
CO	.0
CH ₄	I.0
N	27.7

A careful examination of the pressure reading on the water manometer, analysis of the second sample of gas, and the analysis and amount of gases retained in the solid products shows that the amount of gas retained by the solid products is not sufficient to have any important effect on the observed pressure reading or analysis of the gases.

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